DEVELOPMENT OF AMMONIUM PERCHLORATE BASED SOLID PROPELLANT

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ABSTRACT

There are a lot of development and study of ammonium perchlorate (AP) based solid propellant are already existing in the world. However, there are no detail data and information on the low burning rate AP based solid propellant. This thesis discusses the study of development AP based solid propellant. The objective of the study is to develop low burning rate AP based solid propellant including the selection of a propellant formulation, preparation and development of the propellant, and propellant burning rate experiments with the strand burner at atmospheric pressure. Together with the literature study and theoretical performance, five sets of different mixture were chosen based on their efficiency of propellant mixture. The propellant was a mixture of AP as an oxidizer, aluminum (Al) as fuel and hydroxy-terminated polybutadiene (HTPB) as a binder. For each mixture, HTPB was set at 15% and cured with isophorone diisocyanate (IPDI) (9.33% per weight of HTPB). By changing the AP and Al, the effect of oxidizer- fuel (O/F) ratio on the whole propellant can be determined. The lowest value of the testing obtained are propellant f80, that is 1.47mm/sec with O/F ratio 16.0. The study found, increased ratio O/F will affect to the combustion rate reduction factors of propellant.

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AP	Ammounium Perchlorate
HTPB	Hydroxyl terminated polybutadiene
Al	Aluminum powder
IPDI	Isophorone Diisocyanate
r	Burning rate
a	Empirical constant
P	Pressure
n	Pressure exponent
=	Equal
kg	Kilogram
m^3	Meter cubic
^0C	Degree Celsius
%	Percent
TMO	Transition metal oxide
Fe2O3	Iron oxide
CuO	Copper oxide
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis

CHAPTER 1

INTRODUCTION

1.1 Introduction

Ammonium Perchlorate (AP) is a mixture of materials that have long been used in the production of ballistic missiles, military attack missiles, space applications, and others application. It is known as the powerful oxidizer for the solid propellant. There are two main advantages of Ammonium Perchlorate (AP), stability rocket or bullet resulting in safe and the ability to control the rate of combustion stability in the propellant. [1]

As we know, the study of solid propellant and on Ammonium Perchlorate has done much in this world and has substantial data collected and analyzed. Despite this, there is still no complete and detailed data on Ammonium Perchlorate base on Solid Propellant. This report is a study of Ammonium Perchlorate base on Solid Propellant that covers and include a mixture of methods propellant fuels, burning rate test and the method of preparing and producing solid propellant.

Knowing the limited data and technique used is not enough since other parameters such as the size and type of device used to generate the baseline data is not fully taken into account, then the data cannot be correctly interpreted and errors due to the scale up may result.

The this project, this solid propellant use Ammonium Perchlorate (AP) acting as the oxidant, Aluminum (Al) as fuel and Hydroxy-terminated Polybutadiene (HTPB) as binder/fuel. For the Hydroxy-terminated Polybutadiene (HTPB), there is another mixture contained in the Hydroxy-terminated Polybutadiene (HTPB), namely Isophorone Diisocyanate (IPDI). Isophorone Diisocyanate (IPDI) was calculated based on the percentage of weight of Hydroxy-terminated Polybutadiene (HTPB).

1.2 Objective Study

- To develop low burning rate Ammonium Perchlorate (AP) based solid propellant.

1.3 Research Methodology

The study began with a request for information from literature, journals and books that involve the development of Ammonium Perchlorate based solid propellant. In examining the ways mentioned, the most effective and a lot of help is by referring supervisor and lecturer who has been involved and has had experience in the development of this Solid Propellant based on Ammonium Perchlorate.

After the strand burner test, another measure of the burning rate will be obtained, and the data obtained will facilitate and expedite the process of combustion in the test of propellant later. Lastly, the basic ingredients that commonly used in solid propellants were reviewed.

1.4 Project Methodology

After referring journals and books related, for the first step, the estimated mixture of fuel, oxidizer and binder tested and burned using the easiest and simple method. With a straw, the three types of mixture of materials included in the straw and burnt at open air or normal condition. Each percentage in the test mixture is burnt several times and the average of data will be measured and calculated. For each burning test, the results will be measured burning rate with related tools.

All data obtained from the burning rate test will be collected for the averaging to know the where of mixture percentage is the most efficient.

After getting the data and best results, mix will be tested by applying pressure on the mixture. Given pressure is through by the strand burner (crowford bomb). The purpose of this mixture pressurized is to test the burning rate and to see what reaction this mixture in a high pressure. This is because the mixture should be able to survive and be able to produce a high burning rate in high pressure in the rocket motor.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter describes the details of the study of solid rocket propellant. The information is intended is concerned with the history of solid rocket propellant, ingredients and properties of the propellant, what the function of binder, metal fuel, oxidizer, solid propellant burning rate and burning rate test Equations. With the availability of this literature will surely facilitate the process of conducting experiments burning rate test because all the information is disclosed.

2.2 History Of Solid Propellant Rocket

The history of solid rockets in Japan started from which the Imperial Japanese Navy developed the Funryu (raging dragon) series missiles at its Dai-Ichi Kaigun Koku Gijutsusho (1st Naval Air Technical Arsenal) at Yokosuka, its principal research and development center. Since then, several programs of missile development were carried out through 1945, the end of World War II, in which solid rocket motors were used as propulsion systems. After the blank period of two years, namely in 1947, solid propellant rocket motors were beginning to study again. Research and development of solid rocket motors were directed in two ways, space use and defense use. In space development, many types of solid rocket motors were studied and developed from the successful launch of Pencil rocket in 1955 to the solid rocket motors of H- II rocket and M-V rocket under development.

On the other hand, in defense development, many types of solid rocket motors were also studied and developed from the initiation of 70 mm diameter air to air rocket development to solid rocket motors of various types of rockets and missiles under new development.

Until now, the researches on the history of solid propellant development in Japan were carried out as follows; the paper on the solid rockets in Japan, the papers on the history and status of solid rockets for space use in Japan , the paper on the history of solid propellants for space use in Japan, the papers on the history of solid propellant in Japan, and the paper on the status of solid propellants in Japan. [1]

2.3 Solid Rocket Propellant

Much work has been devoted in various countries to investigating the combustion mechanisms of solid propellants. It is timely to bring together the information obtained by the authors and compared to that of the literature on the combustion of the individual components as well as of their combination into propellants.

The viewpoint adopted here is that of the understanding of the combustion behavior of propellants. Therefore as much information as possible is presented about the fundamentals of the processes (thermal properties, kinetics in the condensed phase and in the gas phase), whereas no attempt is made to establish a complete catalog of practical results on various propellants with different particle sizes, catalysts, variations on the percentage of ingredients. The aim is to give a clear, as conclusive as possible picture. This will then be non compatible with a complete discussion of the various, sometimes contradictory, mechanisms proposed in the literature. Also precluding such a discussion is the will to compare the different components and the corresponding propellants. [2]

There were two types of solid propellants which are homogeneous and heterogeneous propellant. In homogeneous propellant, three main ingredients were combined together with an ionic combination. A common example for homogeneous propellant is a combination of nitroglycerin (NG) and nitrocellulose (NC). Both NC and NG are single base propellant which itself has fuel and oxidizer and could self burning and produce hot gaseous if thermally decomposed. In heterogeneous propellant or sometimes called composite propellant, the basic ingredients are a crystalline oxidizer, metallic fuel and polymeric binder. The term 'composite' states that, the propellant is made at least two different kinds of substances in a heterogeneous mixture, without any chemical bond. [3]

The composite propellants also contain additives to enhance the mechanical strength and alter the burning rate. [4]

Some space is taken up by physical-chemical modeling. The aim is not so much to give the elements of mathematical descriptions which could be used in a priori computation of the burning characteristics of propellants (to the extent that such computations are possible). The point is more to put to test the hypotheses made on the mechanisms of combustion by incorporating them in reasonable models and confronting the results thus obtained with experimental data.

These descriptions can also be viewed, alongside with the data given for each component or propellant, as useful for mastering the regimes of combustion which go beyond stationary combustion, that is erosive burning and unsteady (under pressure excursions or pressure oscillations) combustion responses.

Double-base propellants (made by the extrusion or powder casting techniques) are used in anti-tank rockets or missiles and in some tactical missiles. Their main advantage is that they produce a minimum amount of smoke (only for a small amount of additives).

Composite propellants, based on ammonium perchlorate (AP) without aluminum, generate reduced smoke, HCl and H2O vapor will precipitate into droplets in the plume under given temperature and humidity conditions. They are used for various tactical missiles. With aluminum, they are widely used in missiles and space launchers. They produce alumina smoke, which, in the case of space launchers, could be considered in the future to be undesirable (along with HCl).

Composite propellants based on nitramines and an “active” binder (cross linked polymer with nitroglycerin or other liquid nitrate esters) are used more and more. Without aluminum, they are in the minimum smoke category and they replace DB propellants. With aluminum, they reach the highest specific impulse and density and are used so far for upper stages of strategic missiles. [2]

2.4 Propellant Ingredients And Properties

In a real situation, there are very large numbers of parameters involved in the manufacture of solid propellants including the ingredients and the step of manufacturing. Table 2.1 shows that there would be at least ten different ingredients used in producing solid propellant. While, Table 2.2 shows the common ingredient used in composite solid propellants. Table 2.4.1 shows example ingredients properties of solid propellant.

Table 2.1 Propellant ingredients used by Martin S.M. and Hughes E.H.[5]

Ingredient	**Function**	**Percentages**
Ammonium Perchlorate	Oxidizer	73.00
HTPB	Binder	14.95
Oxamine	Burn rate modifier	5.00
Iron Oxide	Burn rate modifier	2.00
Dioctyl Azelate	Plasticizer	2.00
IPDI	Curing agent	1.40
Zirconium carbide	Ballistic modifier	1.00
Tepanol	Binding agent	0.30
Agerite white	Anti oxidant	0.15
Triphenyl bismuth	Cure modifier	0.10
Magnesium oxide	Cure modifier	0.10
Total		100

Table2.2 Example of the major ingredients in AP based solid propellants

Curing Agent

AP	Al	HTPD	IPDI	References
74.5	-	18.9	1.93	[6]
70.0	18	8.935	0.615	[7]
80.0	-	20.0	1.60	[8]
72.5	15	9.47	0.74	[9]
80.0	-	14.67	1.15	[10]
87.5	-	9.47	0.74	[11]
68.0	18	13.2	0.80	[12]
86.0	-	8.8	-	[13]
73.0	-	21.6	-	[14]
68.0	18	10.085	-	[15]
66.0	16	11.0	-	[16]
67.3	20	10.56	-	[17]
67.5	20	10.6	-	[18]
80.0	-	14.67	1.15	[19]

2.5 Binder

The most important ingredient in solid propellant is a binder. Binder provides the structural glue or matrix in which solid loading are held. The common binder used in solid propellant is elastomeric binders. These binders included polyesters, polysulfide, polybutadiene acrylonitrile (PBAN), carboxyl terminated polybutadiene (CTPB) and Hydroxyl terminated polybutadiene (HTPB).

Composite solid propellants mainly contain a polymeric fuel binder, a metallic fuel such as aluminium (*Al*) powder and an oxidizer usually ammonium perchlorate (AP). The polymeric binder, which constitutes 15-25 wt per cent of the propellant generally consists of a telechelic liquid prepolymer, curing agent, plastisizer, ballistic modifier, bonding agent, and an antioxidant.[20]

Binders provide the structural glue or matrix in which solid granular ingredients are held together in a composite propellant. The raw materials are liquid prepolymers or monomers. The binder impacts the mechanical and chemical properties, propellant processing, and aging of the propellant. Binder materials typically act as a fuel, which gets oxidized in the combustion processes. Commonly used binders are HTPB, CTPB, and NC. Sometimes GAP is also used as energetic binder, which increases the energy density and performance of the propellant. HTPB has been abundantly used in the recent years, as it allows higher solid fractions (total 88–90% of AP and Al) and relatively good physical properties.[23] Composite propellants based on hydroxyl terminated polybutadiene (HTPB) resin are the most widely used solid propellants for launch vehicle and missile applications. [20]

Hydroxyl terminated polybutadiene (HTPB) liquid prepolymers find extensive application as binders in composite solid propellants for launch vehicle technology. The composite solid propellant comprises about 12.20% of polymeric fuel binder, a metal additive such as aluminium powder and an oxidizer, usually ammonium perchlorate. The binder in the solid propellant imparts dimensional stability and structural integrity to the grain and also acts as a fuel during combustion. The mechanical properties of the propellant are largely determined by the extent of polyurethane formation. Hence a knowledge of the kinetics of polyurethane formation will be very useful in the design of propellants, liners, etc., possessing mechanical properties needed for specific purposes.

Table 2.3 HTPB as a polymeric binder [21,22]

Chemical name	Hydroxyl Terminated Polybutadiene (HTPB)
Chemical Formula	$C_{7.075}H_{10.65}O_{0.223}N_{0.063}$ (approximate)
Appearance	Yellowish liquid
CAS No.	69102-90-5
Molecular Weight	NA
Density	989 kg/m^3 [conducted manually]
Boiling Point	300^{0}C
Melting Point	NA
Solubility	Negligible
Stability	Stable under ordinary conditions of use and storage
Conditions to Avoid	Oxidizing condition and extreme temperature

2.6 Metal Fuel

The aluminium powder, from millimetric flakes to nanoparticles, is often used in various applications. A direct link exists between its initial oxidation state and its combustion properties, such as the Minimum Ignition Energy (MIE) and the flame velocity. The nanoscale is often related to propulsion applications and pyrotechnic compounds because of the high burning rate of such small particles due to their high specific contact surface. The nanometric powder also presents the advantage to reduce the waste after combustion [24].

Several facets of this application have been reported, such as production, thermal decomposition in combination with ammonium perchlorate (AP), surface coating of aluminium particles, ignition and oxidation or combustion of aluminium particles including bimodal blends of micrometer and sub-micrometer sized particles, combustion of pressed pellets of aluminium and AP with additives, aluminized composite propellants, and collection of aluminium agglomerates formed during the combustion of aluminized propellants [25].

On the other site, aluminum powder is a high concentration in the earth's crust and relatively high calorific value another perspective energy storage. Unlike hydrogen, it is transportable and easy-to-storage. Aluminum can be used for both energy and hydrogen production. Its oxidation products (aluminum oxide or hydroxide) can be returned to the cycle of aluminum reproduction or used as a vendible product for ceramics, adsorbent, catalyst and other.

One of the main selection criteria for aluminum based energy technology is aluminum oxidation kinetics. Oxidation rate and conversion degree first of all depend on the surface area of initial reagents, the reaction temperature and the type of oxidant [26].

It has been mentioned that depending on the alumina thickness of Al particles, it could be possible to control the explosibility, and so the risk of this powder. The present bench (with the described optimized method for oxidizing the Al powder) will be used in order to provide the required samples with oxide content that are missing. If a given level of safety is wanted for an industrial configuration, this figure can be used to estimate the required oxide content of the Al powder. [24]

2.7 Oxidizer

Properties of ammonium perchlorate in general and particularly its thermal decomposition have been a subject of extensive literature including reviews.

It was revealed during investigation of thermal decomposition of ammonium perchlorate that the process is characterized by a number of features which were purely scientific interest irrespective of applied problems at which these investigations had been aimed at first [27].

Ammonium perchlorate (AP) is one of the main oxidizing agents that have been used in various propellants. The burning behavior of the propellants is highly relevant to the thermal decomposition of AP. Cupric and ferric oxides are proving to be quite effective on thermal decomposition of AP. Several methods have been employed to prepare MOs, such as, solid state reaction, homogeneous precipitation, soil–gel method, citric acid complexion approach and auto-combustion [28].

It is well established that many transition metal oxide (TMO) catalysts including iron oxide (Fe2O3) and copper oxide (CuO) accelerate the decomposition of pure AP. Jacobs and Whitehead summarize the work done to characterize the decomposition of pure AP in the presence of TMO catalyst using various techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), differential thermal analysis (DTA), and mass spectroscopy. In general, it has been shown that both Fe2O3 and CuO lower the ignition temperature of AP, lower the low-pressure deflagration limit, and accelerate decomposition through all temperature regimes. Studies have also investigated the catalytic effect of polymeric binders used in propellants [29].

2.8 Strand Burner

For about 60 years, the industry standard apparatus for routine measurements of linear burning rates has been the so-called strand burner or Crawford bomb proposed by 8 Crawford in 1947. This method, very quick, simple, and economic, is particularly suitable for exploring new propellant compositions, characterizing a propellant's burning rate over a defined pressure and temperature range, or performing quality control of established compositions.

The propellant sample being tested, referred to as a *strand*, is burned within the confines of a pressure tank pressurized with an inert gas. The strand is in the form of a pencil-like stick, and is ignited at one end. The time duration for the strand to burn along its length in a cigarette fashion is measured.

The two basic approaches to economics, experimental characterization of a solid propellant's burning rate are closed and isobaric strand burners. The closed burner technique characterizes the isothermal burning rate function in a continuous manner over a small pressure range with a single burn while the isobaric burner method provides a discrete measurement requiring several burns. Over the years, three major advanced techniques to improve the accuracy of the measurement of the regression rate of strands have been implemented and characterized.

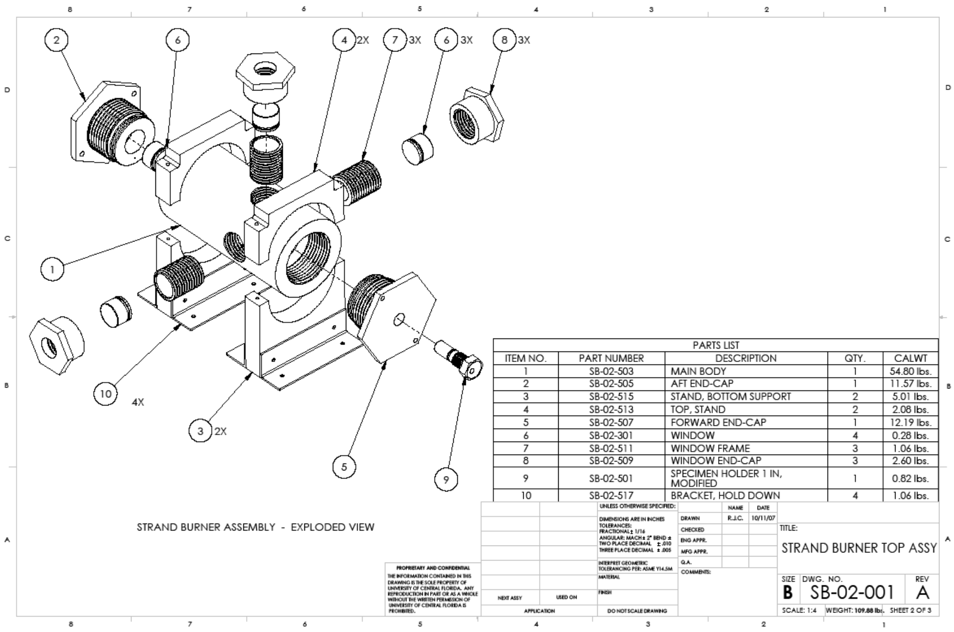

Figure 2.1 Example of Strand Burner [30]

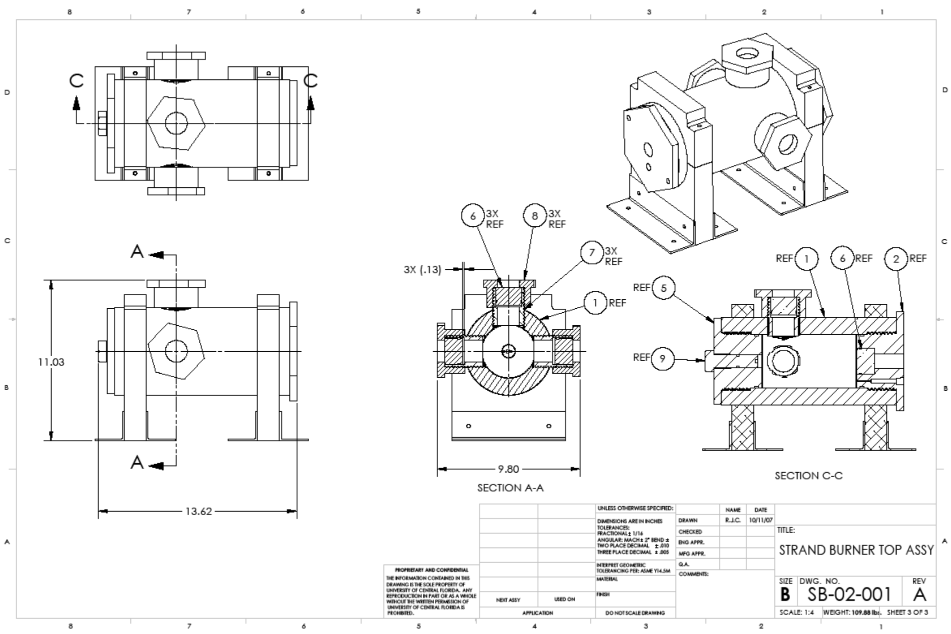

Figure 2.2 Example of Strand Burner [30]

Hermance presented in 1969 a method that consists of using the strand as the dielectric material of a capacitor which forms a part of a resonant inductor-capacitor circuit oscillating at a predetermined center frequency. Bozic et al. Presented the principle of the measurement and data reduction for their method using microwave reflection interferometry in 1995.

Lately, high accuracy internal ballistic measurement has been performed using ultrasonic instrumentation. Actually, the experiment is designed in a fashion that places efficiency and safety at the highest priority [30].

2.9 Solid Propellant Burning Rate Test And Burning Rate Equation

At any instant the burning rate governs the burning time and the mass flow rate of hot gas generated and flowing from the motor combustion chamber to the nozzle and therefore the thrust, and the specific impulse, of the rocket.

The empirical relation relating the burning rate, *r*, and the combustion chamber pressure, *P*, is

$$r = a\, P^n$$

Where *a* is a dimensionless empirical constant influenced by ambient grain temperature (the *temperature coefficient*) and *n* is the *burning rate exponent* also called the *combustion index*. The later is independent of the initial grain temperature and describes the influence of chamber pressure on the burning rate. For stable operation, *n* has values greater than 0 and less than 1.0. High values of *n* give a rapid change of burning rate with pressure and can be determined for the motor.

Measuring rocket propellant burning rates cover various phases (research and technology, screening, development, performance verification, and production control) and each requires suitable tools. Correspondingly, a variety of experimental rigs and procedures is in use worldwide, ranging from the simple strand burners to an array of closed or vented vessels, from different small-scale (or subscale) test motors (ballistic evaluation motors) up to full-scale motors tested first on the ground and eventually in flight conditions [30].

CHAPTER 3

METHODOLOGY

3.1 Introduction

Chapter 3 will discuss the five main factors that influence the selection, preparation and methods of the project. The first step is to select propellant formulation. When getting an accurate formulation, the next step is fabricated propellant strand. With the availability of propellant strand, this will make it easier for preliminary testing at atmospheric condition and burning rate test at pressurize condition. Finally, with the collected data, we can analysis the data easier.

3.2 Selected Propellant Formulation

The selection of propellant type is at the core of any solid rocket motor design. The desirable characteristics of a solid propellant are high specific impulse, predictable and reproducible burning rate and ignition characteristics, high density, ease of manufacturing, low cost, and good ageing characteristics. Propellants should produce low smoke exhaust and not be prone to combustion instability. In addition, they should have adequate thermophysical and mechanical properties over the intended range of operating and storage conditions.

At about this same time, interest also increased in using solid propellants in applications other than missile propulsion. One of the first major uses was jet assisted take off (JATO) as an aid in launching heavily loaded jet bombers [31].This is Typical Propellant Formulation.

Table 3.1 Typical Propellant Formulation [31]

CASTABLE PROPELLANT	
Ingredient	**Weight Per Cent (%)**
Liquid Polymer	10.8
Plasticizer	3.0
Curative	1.0
Metal Powder	16.0
Oxidizer	68.0
Catalyst	1.0
Antioxidant	0.2
	100.0

Table 3.2 Typical Propellant Formulation. [31]

EXTRUDABLE PROPELLANT	
Ingredient	**Weight Per Cent (%)**
Rubber Polymer	12.0
Filler	2.5
Plasticizer	2.5
Curative	0.5
Antioxidant	0.4
Oxidizer	80.0
Catalyst	2.1
	100.0